

Appendix F

Quality Assurance Review – Storm Water Solids Samples

1.0 Introduction

This appendix documents the results of a quality assurance review (QA) of the analytical data for storm water solids samples collected as part of the Terminal 4 Storm Water Project. The data reviewed includes storm water solids sample data from sediment traps deployed from January through June 2007 and September or October through February 2008. The samples were analyzed by Columbia Analytical Services (CAS) of Kelso, Washington and Vista Analytical Laboratory (Vista) or El Dorado Hills, California.

The QA review outlines the applicable quality control (QC) criteria utilized during the data review process, as well as any deviations from those criteria. Examination and validation of the laboratory summary report includes:

- Analytical methods;
- Reporting limits;
- Detection limits and estimated concentrations;
- Sample holding times;
- Custody records and sample receipt;
- Spikes, blanks, and surrogates;
- Duplicates; and
- Calibration and internal standard.

The QA review did not include a review of raw data. Section 2.0 lists the analytical methods used in sample analysis. Section 3.0 defines the QA terms used in this report. Section 4.0 provides the QA results for each sampling event. Section 5.0 lists the qualifiers used in the tabulated results. A list of abbreviations used in this report is included at the end of the document for reference.

2.0 Analytical Methods

Chemical analyses on storm water solids samples consisted of one or more of the following, unless otherwise noted:

- Total Organic Carbon (TOC) by Puget Sound Estuary Program (PSEP) Method;
- Total petroleum hydrocarbons (TPH) as oil and grease (O&G) by EPA Method 1664;
- Total petroleum hydrocarbons as diesel and residual oil by EPA Method 8015M with silica gel cleanup;

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- Metals by EPA Method 6020;
 - Aluminum by EPA Method 6010B;
 - Mercury by EPA Method 7471A;
 - Phthalates by EPA Method 8270C;
 - Organochlorine pesticides by EPA Method 8081;
 - Polychlorinated biphenyl (PCB) Aroclors by EPA Method 8082;
 - Polynuclear aromatic hydrocarbons (PAHs) by EPA Method 8270C SIM; and
 - PCB congeners by EPA Method 1668.

3.0 QA Objectives and Review Procedures

The general QA objectives for this project were to develop and implement procedures for obtaining, evaluating, and confirming the usability of data of a specified quality for monitoring storm water solids collected from the upland storm water conveyance system. To collect such information, analytical data must have an appropriate degree of accuracy and reproducibility, samples collected must be representative of actual field conditions, and samples must be collected and analyzed using unbroken chain-of-custody (COC) procedures.

Reporting limits and analytical results were compared to action levels for each parameter in the media of concern. Precision, accuracy, representativeness, completeness, and comparability parameters used to indicate data quality are defined below.

Reporting Limits. Method reporting limits (MRLs) are set by the laboratory and are based on instrumentation abilities, sample matrix, and suggested MRLs by the U.S. Environmental Protection Agency (EPA) or the Oregon Department of Environmental Quality (DEQ). In some cases, the MRLs are raised due to high concentrations of analytes in the samples or matrix interferences. MRLs are generally consistent with industry standards and below promulgated regulatory standards when possible (if not raised, as discussed above).

Detection Limits and Estimated Concentrations. The method detection limit (MDL) is the lowest quantity of a substance that can be distinguished from the absence of that substance within a stated confidence limit. The MDL is estimated from the mean of the blank, the standard deviation of the blank, and some confidence factor. Performing the sample preparation has potential to underestimate the true MDL.

Holding Times. Holding times are the length of time a sample can be stored after collection and prior to analysis without significantly affecting the analytical results. Holding times vary with the analyte, sample matrix, and analytical methodology used to quantify the analyte's concentration.

Custody Records and Sample Receipt. COC refers to the document or paper trail showing the seizure, custody, control, transfer, analysis, and disposition of physical and electronic evidence. The sample receipt identifies the condition of samples upon arrival at the analytical laboratory.

Method Blanks. A method, or laboratory, blank is a sample prepared in the laboratory along with the actual samples and analyzed for the same parameters at the same time. It is used to assess if detected contaminants may have been the result of contamination of the samples in the laboratory.

Laboratory Control Sample. A laboratory control sample (LCS) is analyzed by the laboratory to assess the accuracy of the analytical equipment. The sample is prepared from an analyte-free matrix that is then spiked with known levels of the constituents of interest (i.e., a standard). The concentrations are measured and the results compared to the known spiked levels. This comparison is expressed as percent recovery.

The LCS analyses for the PCB congeners (completed by Vista) are referred to in the laboratory reports as the On-going Precision and Recovery (OPR) Standard. The laboratory project manager verified that the OPR is equivalent to the LCS.

Laboratory Control Sample Duplicate. In addition, a second laboratory control sample (i.e., the laboratory control sample duplicate [LCSD]) is prepared as above and analyzed. This is compared to the initial laboratory control sample to assess the precision of the analytical method (i.e., relative percent difference [RPD]).

Matrix Spike Analyses. Matrix spike (MS) analyses are performed on samples submitted to the laboratory that are of the same matrix as the actual sample. It is spiked with known levels of the constituents of interest. These analyses are used to assess the potential for matrix interference with recovery or detection of the constituents of interest and the accuracy of the determination. The spiked sample results are compared to the expected result (i.e., sample concentration plus spike amount) and reported as percent recovery.

Laboratory Duplicate. A laboratory duplicate is a second analysis of the QA/QC sample, which serves as an internal check on laboratory quality as well as potential variability of the sample matrix. The laboratory duplicate is analyzed and compared to the primary sample analysis to assess the precision of the analytical method. This comparison can be expressed by the RPD between the original and duplicate samples.

Surrogate Recovery. Surrogates are organic compounds that are similar in chemical composition to the analytes of interest and spiked into environmental and batch QC samples prior to sample preparation and analysis. Surrogate recoveries for environmental samples are used to evaluate matrix interference on a sample-specific basis. Surrogates are organic compounds that are similar in chemical composition to the analytes of interest and spiked into environmental and batch QC samples prior to sample preparation and analysis. Surrogate recoveries for environmental samples are used to evaluate matrix interference on a sample-specific basis.

The surrogate recovery analyses for the PCB congeners (completed by Vista) are referred to in the laboratory reports as the Internal Standard (IS). The laboratory project manager verified that the IS recovery percentages are equivalent to the surrogate recovery percentages.

Field Duplicate. A field duplicate is a second field sample collected from a selected monitoring well. Field duplicate samples serve as a check on laboratory quality as well as potential variability of the sample matrix. The field duplicate is analyzed and compared to the first sample to assess the precision of the analytical method. This comparison can be expressed by the RPD between the original and duplicate samples.

Calibration. Satisfactory instrument calibration is established to confirm that an instrument is capable of producing acceptable quantitative data. An initial calibration verification (ICV) demonstrates that the instrument is capable of acceptable performance at the beginning of an experimental sequence. Continuing calibration verifies (CCV) that the daily performance of the instrument is satisfactory.

Internal Standard. An internal standard is a chemical substance that is added in a constant amount to samples, the blank, and calibration standards in a chemical analysis. This substance is then used for calibration by plotting the ratio of the analyte signal to the internal standard signal as a function of the analyte concentration of the standards. This is done to correct loss of analyte during sample preparation.

4.0 QA/QC Review Results

Based upon sample volume availability, the samples were analyzed for one or more of the following: TOC, TPH, metals, aluminum, mercury, phthalates, organochlorine pesticides, PCB Aroclors, PCB congeners, and PAHs using the methods listed in Section 2.0.

Reporting Limits. Elevated MRLs of analytes consisted of the following:

- Organochlorine Pesticides: All of the analyte MRLs were raised. The samples would not filter prior to GPC cleanup. The MRL is further elevated for several analytes in all field samples. The chromatogram indicated the presence of non-target background components. The matrix

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- interference prevented adequate resolution of the target compounds at the MRL. The results were flagged with an "i".
- Phthalates: The reporting limits were elevated for samples Basin L, Basin D, and Basin T. The sample extract was diluted prior to instrumental analysis due to relatively high levels of non-target components. Cleanup of the extracts was performed within the scope of the method but did not eliminate enough of the background components to prevent dilutions.
 - TPH: The reporting limits for diesel-range and residual-range TPH for sample Basin L were raised due to dilution and less than optimal sample volume. Both analytes were detected in the sample at concentrations above the reporting limit.

The MRLs for some organochlorine pesticides, phthalates, and PCB Aroclors were higher than the applicable screening level. These values are highlighted yellow.

Detection Limits and Estimated Concentrations. Several estimated MDLs and concentrations were identified as follows:

- Estimated non-detect concentrations, sample-specific MDL, calculated for selected non-detected analytes:
 - PCB Congeners: Flagged with an asterisk.
- Estimated detected concentrations below the lower calibration limit of the instrument:
 - PCB Congeners: Flagged with a "J" qualifier for some analytes for all samples.
- Estimated detected concentrations that are below the MRL and above the MDL:
 - Phthalates: Flagged with a "J" qualifier.
 - Organochlorine Pesticides: Flagged with a "J" qualifier.
 - PCB Aroclors: Flagged with a "J" qualifier.
 - PCB Congeners: Flagged with a "J" qualifier.

Holding Times. No holding times were exceeded.

Custody Records and Sample Receipt. Samples were received consistent with the accompanying COC. Upon receipt by the laboratory, storm water solids samples were initially frozen and kept at a temperature of -20 degrees Celsius (°C). Once the final set of storm water solids samples was submitted to the lab, the archived frozen samples for each basin were composited and stored in a refrigerator at -4 °C.

Method Blanks. The results from the method blanks are summarized in the following table.

Analysis	Analyte	Concentration
Metals	Chromium	0.11 mg/kg
	Lead	0.03 mg/kg
	Nickel	0.03 mg/kg
	Zinc	0.4 mg/kg
Organochlorine Pesticides	Methoxychlor	0.32 µg/kg
PAHs	Naphthalene	1.5 µg/kg
	Indeno (1,2,3-cd) pyrene	0.17 µg/kg
PCB Congeners	PCB-77	1.96 ng/kg

No analytes were detected at concentrations less than or equal to five times the detected concentration from the method blanks. Therefore, none of the associated data was flagged.

Laboratory Control Sample. Percent recoveries of the LCS were within control limits for TOC, metals, phthalates, O&G, PCB Aroclors, PCB congeners, PAHs, and organochlorine pesticides.

Laboratory Control Sample Duplicate. Percent recoveries and RPDs of the LCSD were within control limits for TOC, O&G, organochlorine pesticides, PCB Aroclors, phthalates, and PAHs. There was no LCSD analyzed for metals and PCB congeners.

Matrix Spike Analyses. Percent recoveries of the MS were within control limits for TOC, metals, and phthalates. There was no MS analyzed for organochlorine pesticides, O&G, PCB Aroclors, PCB congeners, and PAHs. In some cases, this was due to insufficient sample volume to perform an MS/MSD. An LCS/LCSD was reported in lieu of the MS/MSD for these samples.

Matrix Spike Duplicate Analyses. The RPD of the MSD was within control limits for phthalates. There was no MSD analyzed for TOC, metals, organochlorine pesticides, O&G, PCB Aroclors, PCB congeners, and PAHs.

Laboratory Duplicate. The laboratory duplicate for metals was within quality control limits, except antimony. The duplicate RPD criterion of +/-30 percent was exceeded for antimony in the laboratory duplicate. The associated results are flagged with a "J2" qualifier. The laboratory case narrative attributed the variability of the duplicate results to the heterogeneous character of the sample.

The laboratory duplicate for phthalates was within quality control limits, except Dimethyl Phthalate and Bis(2-ethylhexyl) Phthalate. The duplicate RPD criterion of +/-30 percent was exceeded for Dimethyl Phthalate and Bis(2-ethylhexyl) Phthalate in the laboratory duplicate. The RPD criterion is not applicable to Dimehtyl Phthalates, because the concentrations for the primary and duplicate samples are between the MRL and MDL and are already flagged with the "J" qualifier, indicating the concentrations are estimated. The results for the primary and laboratory duplicate for Bis(2-ethylhexyl) Phthalate are flagged with a "J2" qualifier. The laboratory case narrative attributed the variability of the duplicate results to the heterogeneous character of the sample.

The laboratory duplicate for PAHs was within quality control limits, except for anthracene, benzo(a)pyrene, fluoranthene, and naphthalene. The duplicate RPD criterion of +/-30 percent was exceeded in the laboratory duplicate. The associated results are flagged with a "J2" qualifier. The laboratory case narrative attributed the variability of the duplicate results to the heterogeneous character of the sample.

The laboratory duplicate for organochlorine pesticides was within quality control limits, except for 2,4'-DDE. The duplicate RPD criterion of +/-30 percent was exceeded for 2,4'-DDE in the laboratory duplicate. The RPD criterion is not applicable to 2,4'-DDE, because the concentrations for the primary and duplicate samples are between the MRL and MDL and are already flagged with the "J" qualifier, indicating the concentrations are estimated. In addition, DDT, DDD, and DDE were detected in the duplicate sample and were not detected in the primary sample. The laboratory case narrative notes that "while it is clear that in the replicate sample that there are detections for these analytes, in the parent sample there are interferences preventing adequate resolution of these peaks in the chromatogram". Please see the section above regarding reporting limits for additional explanation. The non-detect results in the primary sample have been flagged with the "i" qualifier.

Surrogate Recovery. All surrogate recoveries were within quality control limits except for the surrogate recoveries for phthalates in samples Basin L and Basin T. The laboratory case narrative noted that the analysis of the samples required dilution, which resulted in surrogate concentration below the MRL and that no further corrective action was appropriate.

Calibration. Below is documentation of calibration outliers during the analysis of the samples.

- Organochlorine Pesticides: The primary evaluation criterion was exceeded for Mirex in two of the CCVs. The alternative evaluation specified in the EPA method was performed using the average percent recovery of all analytes in the verification standard.

Results for Mirex in the LCS and LCSD have been reported from a column using average percent recovery of all analytes in the verification standard.

At least one analyte in the Basin L, Basin M, and Basin T samples was flagged with the "P" qualifier, indicating that the instrument confirmation criteria were exceeded. The case narrative

noted that the higher of the two values is reported when both peaks were within the expected retention time window for this analysis and Gaussian in shape, or the lower of the two values was reported when there was an apparent interference on the alternate column that produced the higher value. A subset of samples were flagged with the qualifier "JP", indicating that the aforementioned confirmation comparison criteria are not applicable because at least one of the values is below the MRL.

- PCB Aroclors: The result for Aroclor 1254 for sample Outfall 53 was flagged with the "JP" qualifier. This indicates that the instrument confirmation criteria were exceeded. However, because the value is below the MRL, the aforementioned confirmation comparison criterion is not applicable.

At least one analyte in the Basin L, Basin M, and Basin T samples was flagged with the "P" qualifier, indicating that the instrument confirmation criteria were exceeded. The case narrative noted that the higher of the two values is reported when both peaks were within the expected retention time window for this analysis and Gaussian in shape, or the lower of the two values was reported when there was an apparent interference on the alternate column that produced the higher value. A subset of samples were flagged with the qualifier "JP", indicating that the aforementioned confirmation comparison criteria are not applicable because at least one of the values is below the MRL.

Other. Below are Case Narrative notes that apply to specific analyses or analytes.

- PCB Congeners: The case narrative noted that when mixtures of PCB Aroclors are present in a sample, correct identification and quantitative analysis of the individual Aroclors can be subjective, in particular when differentiating between Aroclor 1242 and 1248. The laboratory conducted a review of the sample chromatograms in a number of samples where three PCB Aroclors were detected and the chromatograms indicated the presence of PCB patterns that spanned the entire elution range from Aroclor 1242 to Aroclor 1260. The laboratory noted that when Aroclor mixtures are present in a sample, care is taken to minimize the possibility of double-counting PCBs, but the potential exists for a high bias from contribution of one Aroclor to another due to common peaks or peaks that cannot be completely resolved.

5.0 Qualifiers

Below is a list of all qualifiers used on the tabulated results of the storm water solids analyses.

5.1 Universal Qualifiers

- # = The control criteria is not applicable. See Case Narrative.
- i = The MRL/MDL has been elevated due to matrix or chromatogram interference.
- J2 = The analyte was positively identified; the resulting concentration is an estimated value. The RPD exceeded the precision goal from the field or laboratory duplicate.

5.2 Inorganic Qualifiers

- J = The result is an estimated concentration that is less than the MRL but greater than or equal to the MDL.

5.3 Organic Qualifiers

- P = The GC or HPLC confirmation criteria was exceeded. The relative percent difference is greater than 40 percent between the two analytical results.
- J = The result is an estimated concentration that is less than the MRL but greater than or equal to the MDL.
- H = The chromatographic fingerprint of the sample resembles a petroleum product, but the elution pattern indicates the presence of a greater amount of heavier molecular weight constituents than the calibration standard.
- O = The chromatographic fingerprint resembles an oil, but does not match the calibration standard.

5.4 PCB Congener Qualifiers

- J = The amount detected is below the Lower Calibration Limit of the instrument.
- * = Sample-specific detection limit (DL) in the MRL column. DLs were calculated for non-detected congeners.

Abbreviations:

CAS = Columbia Analytical Services
CCV = Continuing Calibration Verification
COC = Chain-of-Custody
DEQ = Oregon Department of Environmental Quality
DL = Sample-Specific Estimated Detection Limit
EPA = U.S. Environmental Protection Agency
ICP-MS = Inductively Coupled Plasma – Mass Spectroscopy
ICV = Initial Calibration Verification
IS = Internal Standard
LCS = Laboratory Control Sample
LCSD = Laboratory Control Sample Duplicate
MDL = Method Detection Limit
µg/kg = Micrograms per Kilogram
MRL = Method Reporting Limit
MS = Matrix Spike
MSD = Matrix Spike Duplicate
ng/kg = Nanograms per Kilogram
O&G = Oil and Grease
OPR = On-going Precision and Recovery Standard
PAH = Polynuclear Aromatic Hydrocarbon
PCB = Polychlorinated Biphenyl
pg/kg = Picograms per Kilogram
PSEP = Puget Sound Estuary Program
QA/QC = Quality Assurance/Quality Control
RPD = Relative Percent Difference
TOC = Total Organic Carbon
TPH = Total Petroleum Hydrocarbon
Vista = Vista Analytical Laboratory

